SCIENCE FOR CERAMIC PRODUCTION

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COMPARATIVE EVALUATION OF REFRACTORIES USED IN FIRING OF PORCELAIN AT THE GZHEL' JOINT-STOCK COMPANY

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It is demonstrated that the uniform distribution of silicon carbide with a homogenous granular composition throughout the volume of the material makes it possible to reduce thermal stresses and to increase the turnover of refractories.

In firing fine ceramic articles (porcelain and faience), saggers, trays, plates, and other refractory parts are used to fill the kiln space and to improve the product quality. The following requirements are imposed on saggers and plates: high strength ensuring resistance to mechanical impacts in charging and discharging of the product; high thermal resistance; sufficient homogeneity of the structure and density to prevent break-off of the filler grains and their fusion with the glazing of the product.

The intensification of fine ceramic firing is often impeded by the insufficient heat stability of saggers and plates. An especifically negative effect is caused by abrupt fluctuations of the TCLE due to the polymorphous transformations of some oxides and compounds, for instance, that of quartz existing in free form. The heat resistance of refractories is influenced by the size and shape of grains, the amount and the composition of the liquid phase formed in the course of firing, and the porosity of articles.

The deterioration of service conditions of refractories related to intensification of the firing process determines the selection of the main materials for the manufacture of refractory parts: mullite, silicon carbide, and, to a lesser extent, chamotte materials, although the latter are still widely used in the industry [1, 2].

The Gzhel' JSC is still using different types of refractories produced by slip casting and plastic molding.

Chamotte mixtures on a clay binder have received the widest acceptance as refractory mixtures for producing saggers and other refractory products for porcelain and faience firing due to its availability and low cost and the simplicity of this technology. The refractories currently used contain 70 – 75% chamotte [3], although it requires rather high molding pressure. Unfortunately, the heat resistance of these articles as a rule is low (not more than 5 – 6 cycles). Such refractories have a mean density of 1.75 – 1.90 g/cm^3, water absorption of 14 – 17%, compressive strength of 15 – 22 MPa, bending strength of 8 – 12 MPa, softening start temperature under 0.2 MPa loading equal to 1320 – 1360°C, and TCLE of (5 – 7) × 10°C.

Chamotte is introduced in refractory mixtures as a grog component, which has a favorable effect on the behavior of mixtures in drying. Furthermore, the use of broken sagger waste as the chamotte component makes it possible to significantly reduce the consumption of scarce materials and decrease the cost of sagger production. However, sagger waste has primarily to be sorted to remove overburned and fused lumps and periodically has to be renewed by using virgin chamotte. The use of recycled chamotte leads to a significant decrease of the heat resistance of the product due to the accumulation of cristobalite in the material. The renewal of the chamotte component in a refractory mixture by means of introducing virgin chamotte (at least 40% of the total quantity of chamotte in the mixture) is obligatory. By varying the ratio between different chamotte fractions in a mixture, one can reduce the shrinkage of the mixture in drying and firing and obtain a porosity of 8 – 12% in the material, which best satisfies the requirements imposed on the strength and the heat resistance of refractories.

To improve the quality and to extend the service life of refractories, such additives as alumina, silicon carbide, etc. are introduced into mixtures.

Until recently, the Gzhel' JSC used a technology of plastic molding of saggers from chamotte mixtures with a technical alumina additive. In view of the continuous increase in

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material prices, such production becomes economically inadvisable.

A decrease in the content of the fine fraction in high-chamotte mixtures and its partial replacement by electrocorundum makes it possible to increase by 1.3 – 1.5 times the turnover of the refractories. At the same time, the bending strength grows to 13 – 15 MPa, the compressive strength grows to 45 – 49 MPa, and the softening start temperature under 0.2 MPa loading is within the limits of 1420 – 1430°C.

The slip method for mixture preparation with subsequent casting in gypsum molds is used for making thin-walled saggers with a uniform thickness of the walls and the bottom.

Silicon carbide mixtures have an increased content (48 – 99%) of SiC. Silicon carbide refractories on a clay binder can be used up to a temperature of 1450°C. They are 2.5 – 3 times stronger than the chamotte refractories, which makes it possible to produce articles with thinner walls and increase the useful load of the furnace space. The high thermal conductivity of such refractories decreases the temperature difference across the furnace and makes it possible to shorten the time of heating and cooling of fired articles and to improve their quality. However, the clay binder prevents full use of the valuable properties of silicon carbide.

Taking into account the conditions of service of saggers, special attention should be paid to increasing their heat resistance while preserving a sufficiently high mechanical strength. Therefore, it was proposed to exclude chamotte from the mixture composition and instead to introduce a material with a low TCLE, high thermal conductivity, and high resistance to furnace gases. Silicon carbide is precisely such a material, which makes it possible to produce a sagger fit for 100 cycles or more, depending on the production method.

It was decided at the Gzhel' JSC not to create additional facilities but to make use of the existing slip casting technology and to produce carborundum-bearing saggers of various standard sizes by casting in gypsum molds.

Mixtures with a silicon carbide content of 30 and 55% were used for saggers. The size of SiC grains did not exceed 125 μm. The slip moisture was 30 – 36%. The articles were fired at temperatures of 1320 and 1410°C. Chamotte saggers were produced for reference purposes, and other reference samples were articles made by plastic molding at the Dulevo Porcelain Factory with a silicon carbide content of 45% and articles made by Anna Werke (Germany) by semidry molding with a silicon carbide content of 55%.

The structure of the articles before and after service was analyzed on polished sections employing an Omnimet image analyzer for a quantitative evaluation of the product quality. This method made it possible to determine the approximate percent content of the component phases (crystalline, vitreous, and gaseous) and to obtain their parameters (length, width), shape (elongated, rounded), and orientation.

Chamotte refractories made by Gzhel' JSC. These saggers were cast in gypsum molds from a chamotte-based slip [4]. After firing at 970 – 980°C the articles were engobed and fired again at 1320°C.

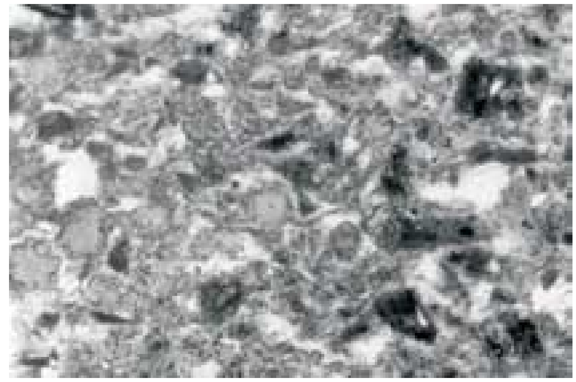

Fig. 1

Fig. 2

The structure of the material is heterogeneous (Fig. 1). The material exhibits quartz grains of fragmental shape with maximum size up to 100 – 120 μm in the amount of about 12%. There are alumina grains up to 60 – 100 μm in size and many dark aggregates of fragmental shape, whose boundaries are weakly visible. These aggregates are nearly isotropic and occasionally contain fine quartz grains up to 15 – 20 μm and an insignificant quantity of needle-shaped mullite of size 10 – 12 μm. These aggregates are presumably the residues of chamotte grains that have not entered into the reactions; fine pores (up to 50 μm), isolated ones or two pores merged as a dumbbell, are often visible in these aggregates. The pores are largely of an irregular shape. Fine pores are often merged into associations up to 200 – 250 μm. The pore content reaches 20%. The total number of chamotte in the mixture varies within the limits of 40 – 45% with an average grain size of 51 μm. The vitreous phase is present in the amount of 20 – 23% and is homogeneously distributed in the volume.

Saggers made from slip containing 55% silicon carbide. The structure of this material is rather heterogeneous (Fig. 2). There are many silicon carbide grains of fragmental shape up to 120 – 180 μm in size with an average size of 40 μm. The silicon carbide content reaches 46%. Occasionally quartz grains up to 100 μm are found with an average size of 36 μm, and the quartz content is 1 – 2%. Alumina

Fig. 3

Fig. 4

is represented by corundum (9 – 11%) of size up to 100 μm and a mean size of 37 μm.

The pores have an irregular isometric shape with a maximum size of 180 – 200 μm and an average size of 15 μm. The pore amount is within the range of 15 – 20%.

The vitreous phase content reaches 22 – 25%. The vitreous areas have heterogeneous compositions and different tints. Occasionally anisotropic inclusions and fine pores around 50 μm are found in the glass.

Thus, the structure of this article has a rather homogeneous grain distribution and a homogeneous granular composition of silicon carbide and corundum. The vitreous phase ensures good adhesion of corundum and silicon carbide grains in the presence of sealed, rather isometric pores.

Saggers made from slip containing 30% silicon carbide. The structure of this material is rather homogenous (Fig. 3). The silicon carbide content is 32% with a maximum grain size of 200 μm and a mean size of 41 μm. The silicon carbide grains are fragmental and elongated.

Chamotte was introduced in the composition of this mixture, and dark isotropic sites with blurred boundaries and with mullite needles 5 – 10 μm long are visible at sites where chamotte used to be. The content of such sites is around 25% with a maximum size of 200 μm and a mean size of 32 μm.

The quartz content reaches 6% with a maximum grain size of 120 μm and a mean size of 14.6 μm. The corundum grains observed have an isometric shape and a maximum size of 100 μm and a mean size of 28.5 μm; the content of corundum in the mixture is 13.5%.

The vitreous phase in the amount of 20 – 23% is rather homogeneous and well extended.

The porosity of the article is 21%, the maximum pore size 200 – 250 μm, and the mean size 16 μm. The pores are mostly elongated with irregular edges.

Thus, this material has a well-extended vitreous binder ensuring good adhesion of all components of the mixture and a sufficiently high strength. The pores in this material are slightly larger than in the material with 55% silicon carbide.

Saggers based on silicon carbide made at the Dulevo Porcelain Factory. The structure of the material is heterogeneous and coarse-grained (Fig. 4). The article contains very large silicon carbide grains, up to 1000 – 2000 μm with a mean size of 170 μm, and quartz grains of size 60 – 80 μm and fine silicon carbide grains are located between the former. The silicon carbide content is 38%, All grains have a fragmental shape, and sometimes their surface is corroded. In this case an argillaceous material acts as a binder. The content of corundum grains with a mean size of 48 μm reaches 10%.

The pores are fissured, large, and mostly irregular. Occasional pores have the shape of elongated cracks emerging at different angles. The pore size reaches 1000 μm with a mean size of 59 μm. The fired material porosity is 28 – 30%. Fine pores are found in the vitreous mass that interconnects the large silicon carbide grains. The amount of the vitreous phase reaches 20 – 22%.

Thus, the products of the Dulevo Porcelain Factory are distinguished by large silicon carbide grains and large pores that sometimes form cracks of considerable sizes. The amount of the vitreous phase is insufficient to fill the intergranular space and, as a consequence, does not ensure good adhesion of the grains of silicon carbide, which is an inert filler.

Saggers made by Anna Werke. The content of silicon carbide grains in the material reaches 51%, and their maximum size is 1000 – 2000 μm with a mean size of 320 μm (Fig. 5). Sometimes silicon carbide grains are corroded. Few fine grains are observed. The space between the large grains is filled with a vitreous mass and fine silicon carbide grains (12 – 40 μm).

The pores are represented by cracks and elongated cavities, most often located inside the mass and not along the boundaries of the silicon carbide grains. The sizes of the cracks and cavities are, respectively: maximum length 500 – 1000 μm and width of 100 – 150 μm. The pore content is equal to 15% with an average pore size of 73 μm.

Comparing the structure of this article and that of the Dulevo article, it should be noted that the present sample contains fewer large silicon carbide grains and a higher content of fine grains. This sample has a higher density and

Fig. 5

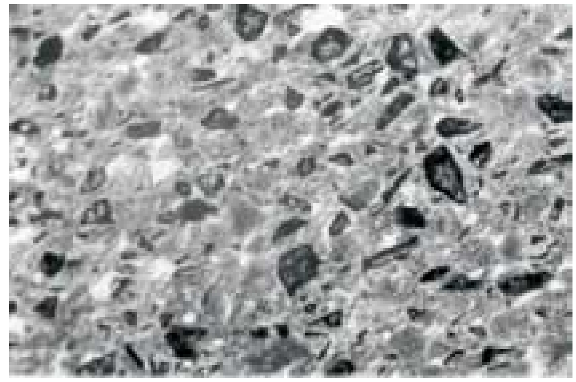

Fig. 6

strength due to the homogeneous distribution of the vitreous phase in the volume.

Saggers containing 55% silicon carbide after 50 cycles. The content of silicon carbide grains in the material is around 31%, the maximum grain size reaches 120 – 150 μm, and the mean size is 34.6 μm. Silicon carbide grains exhibit an edge around 2 μm thick (Fig. 6). Quartz grains are observed in an insignificant quantity (around 1%) with a maximum size of 100 – 120 μm. They also have an edge around 2 μm thick, which is probably due to their fusion. The content of corundum grains is 10%, their maximum size is 60 – 90 μm, and the mean size is 23.5 μm. The grain boundaries do not have clear contours.

The pores are elongated with an irregular shape, a maximum length of 80 – 100 μm, and a mean length of 14.5 μm. The porosity is 20%.

The vitreous phase is represented by glass with homogeneous fine crystallization.

A comparison with the initial sagger sample revealed the decreased content of silicon carbide due to its oxidation and the presence of an edge on the surface, which, according to x-ray phase analysis, correlates with cristobalite. The glass binder in this sample, as a result of crystallization, has a rather homogeneous structure and tinting, and alumina grains are replaced by certain formations of a dark yellow or a yellow-brown color.

Service of saggers and other refractories. The turnover of saggers is lower than that of other refractory products (plates, props) due to their more complex configurations. The destruction of a sagger, as a rule, starts with a crack originating in a lateral wall and then propagating and opening toward the bottom.

A crack is produced by thermal stresses arising due to the differences in the TCLEs of the individual solid phases. Introduction of silicon carbide in the mixture makes it possible to decrease the thermal stresses, since the TCLE of silicon carbide is lower than the TCLE of chamotte, and a higher thermal conductivity increases the heat resistance of the article. All this enhances the turnover of the refractory.

Saggers made by the Dulevo Factory and by Anna Werke have approximately equal contents and sizes of silicon carbide grains, but the turnover of these articles differs. Anna Werke saggers last twice as much, which can be accounted for by the more uniform distribution of silicon carbide grains in the mixture. The fissured pores in this case are located not along the grain boundaries but throughout the mixture. Accordingly, the thermal stress is insignificant and does not cause crack opening.

Saggers produced by the Gzhel' JSC that were cast from aqueous slips have demonstrated good service results (turnover more than 50 cycles) and continue to be used. Saggers made at the Dulevo Porcelain Factory served a little more than 20 cycles. The structure of the Gzhel' saggers consists of finer silicon carbide grains with a homogeneous distribution, which determines their increased strength and heat resistance.

The turnover of the chamotte saggers lasted 3 – 5 cycles. After 1 – 3 cycles, a crack originated on the lateral side of a sagger and after another 2 – 3 cycles it was opened to the bottom, and the article was destroyed. It was observed that when sagger waste was replaced by virgin chamotte, the turnover increased. The crack originated only after 4 – 5 cycles. Apparently this process is related to the formation of cristobalite, which in cooling generates substantial thermal stress and destroys the sagger.

Thus, dense saggers containing silicon carbide and cast from an aqueous slip in gypsum molds at the Gzhel' Company have a high turnover (over 50 cycles), which is determined by the homogeneous distribution of sufficiently fine silicon carbide grains and glass in the bulk of the material.

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